CONTINUOUS DEWAXING OF OILS BY IN SITU REFRIGERATION

Inventor: Leslie R. Gould, Sarnia, Ontario, Canada

Assignee: Esso Research and Engineering Company

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Primary Examiner—Herbert Levine
Attorney—Pearlman and Stahl

ABSTRACT

An improved process for dewaxing petroleum oil stocks. Feed oil, with or without a dewaxing solvent, is both mixed and cooled by direct contact with boiling liquid refrigerant, with required residence time in a vessel containing sufficient stages to effect required wax crystal growth.

17 Claims, 2 Drawing Figures
CONTINUOUS DEWAXING OF OILS BY IN SITU REFRIGERATION

CROSS-REFERENCE TO RELATED APPLICATIONS
This is a streamlined continuation of application Ser. No. 829,467, filed June 2, 1969, now abandoned.

BACKGROUND OF THE INVENTION
This invention relates to an improved process for effecting the removal of wax from wax-containing materials. More particularly, this invention relates to the dewaxing of wax-containing materials, such as waxy petroleum distillate fractions and/or waxy deasphalted residua such as bright stock, wherein the precipitation of the wax is achieved by direct contact with a liquid refrigerant. Still more particularly, this invention relates to a process wherein a wax-containing petroleum oil stock is precipitated by direct contact with a boiling liquid refrigerant. Still more particularly, this invention relates to a process wherein a wax-containing petroleum oil stock, with or without dewaxing solvent, is both mixed and cooled by direct contact with a boiling liquid refrigerant.

DESCRIPTION OF THE PRIOR ART
It is known in the art to dewax petroleum oil stocks utilizing a large number of different batch processes in which liquid propane or other similar normally gaseous hydrocarbons are employed as a diluent and internal direct refrigerant. In these batch type processes, commonly known as "Propane Dewaxing" processes, the refrigeration and precipitation of wax is effected by vaporizing a portion of the liquid diluent, or refrigerant, in which the oil stock is dissolved. The vaporization can be accomplished merely by reducing the pressure in the vessel containing the wax-containing petroleum oil stock and the liquid refrigerant. That is, the pressure reduction causes the volatile, normally gaseous liquid refrigerant to boil, or vaporize. Thus, the main body of liquid supplies the latent heat of vaporization to the refrigerant, and the temperature of this liquid is thereby lowered. The pressure is lowered at least to the point corresponding to a temperature at which the wax dissolved in the petroleum fraction is precipitated out as wax crystals. After this desired temperature is reached, the solution with the suspended particles of wax is then filtered and the dewaxed oil is recovered. The refrigerant to oil ratios employed in such a process are dependent upon the particular oil and refrigerants employed and can be adjusted to facilitate the easy handling of the wax slurry and optimum filtration rates.

These dewaxing processes which involve the step of vaporizing a portion of the diluent in contact with the mixture being chilled have been reasonably successful, but the vaporization produces an intense agitation of the mixture which has in the past been considered quite detrimental, by preventing crystal growth and breaking up already formed wax crystals into smaller units. It has been considered that oil stocks containing small crystals are much more difficult to handle in the wax separation stage than are stocks containing large crystals. The size of crystals is controlled by the rate of cooling of the oil, wax and diluent. The lower the rate of cooling, the better the filterability of the crystal matrix and the lower the oil content of the crystals. Although not intended to limit the scope of this invention, a practical rate of cooling of the oil, wax and diluent is 1°F. to 5°F. per minute.

It has been necessary in these "propane dewaxing" plants to employ batch chilling in order to prevent the flashing of propane at a point of pressure release, with consequent shock chilling. In addition, "propane dewaxing" has been carried out with the addition of a dewaxing solvent.

It is also known in the art to dewax petroleum oil stocks by cooling an oil-solvent solution in a scraped surface exchanger. In this type process, commonly known as the "Solvent" or "Ketone Dewaxing" process, the oil and a selective solvent are admitted at a temperature sufficient to effect thorough solution of the oil in the solvent. The extent of dilution is again dependent upon the particular oil and the particular solvent employed and can be adjusted to facilitate easy handling and optimum filtration rates. The solution is then cooled at a uniformly slow cooling rate; e.g., 1°F. to 5°F. per minute, under conditions which are controlled so as to avoid any substantial agitation of the solution during precipitation of the wax. Notwithstanding the carefully controlled conditions used in this type process, there are several deficiencies which hamper commercial operation. Most significant among these deficiencies is the loss of good heat transfer due to wax deposition on the exchange surfaces. Such fouling has been repeatedly noted after short periods of operation; e.g., 24 to 48 hours. Associated directly with the loss of good heat transfer is the loss of careful control over the cooling rate and the corresponding loss of uniform crystal growth. This non-uniform crystal growth then results in lower filtration rates. The high pressure drop through the chilling section also reduces the maximum feed rate obtainable. Another problem which has arisen is that with certain types of oil stocks, for example those containing a mixture of paraffin and microcrystalline waxes, extremely poor filter rates are obtained, presumably due to the formation of wax crystals which are difficult to separate from the oil. A concomitant of this difficulty is that the oil content of the wax is generally at a level which is undesirably high, and in turn results in poor yields of dewaxed oil. The solvents employed in these ketone dewaxing processes are ketones containing from three to six carbon atoms, including such solvents as methyl ethyl ketone, acetone, methyl isobutyl ketone, methyl propyl ketone or mixtures thereof, and they may be in combination with an aromatic compound, such as benzene, toluene, petroleum naphtha or mixtures thereof.

It is also known in the art to dewax petroleum lubricating oils with hydrocarbon solvents in a two-step process. In the first step, an oil-solvent solution is cooled to a temperature just above that at which the wax begins to precipitate. In the second step, the wax is precipitated upon further cooling of the solution by incremental addition of prechilled solvent along the height of a vertical tower. Prechilling of the oil-solvent solution prior to use of internal cooling by incremental addition of solvent is taught as a step essential to the avoidance of the detrimental effects of shock chilling. Moreover, as in the external cooling processes, the
prior art teaches that any degree of substantial agitation should be avoided during the wax precipitation step. The principal disadvantages of this type process are the expense and operating problems associated with the required separate oil-solvent blending equipment and the additional heat exchange equipment employed in the first cooling step. It is also felt that a certain amount of shock chilling still occurs in this type process with resultant lower filter rates and yields.

BRIEF SUMMARY OF THE INVENTION

It has now been found that the foregoing deficiencies can be avoided with the dewaxing process of the present invention. Accordingly, it is an object of this invention to provide a Propane Dewaxing process which may be operated continuously. A further object of this invention is to provide a Solvent or Ketone Dewaxing process which can be carried out without the necessity of utilizing external cooling with boiling liquid refrigerant in the shell of a scraped surface exchanger. Another object of this invention is to provide a dewaxing process wherein internal or in situ cooling is utilized without the need of a separate mixing facility or a solution precooler. Still another object of this invention is to provide a dewaxing process which affords a controlled rate of crystallization. A still further object of this invention is to provide a dewaxing process wherein improved filterability of the slurry can be obtained. Another object of this invention is to provide a dewaxing process wherein the area of filtration required may be reduced. Yet another object of this invention is to provide a dewaxing process wherein an improved yield of dewaxed oil may be obtained by a reduction in the quantity of oil which becomes occluded in the wax crystals. Yet another object of this invention is to provide a dewaxing process wherein lower temperatures of crystallization, and thus a lower pour product, is obtained with a given refrigeration system operation. Another object of this invention is to provide a dewaxing process which would require a lower capital investment and lower operating cost. Other objects will be apparent from the following description.

According to this invention, the foregoing and other objects are accomplished by mixing and cooling a petroleum oil stock, in a vessel or vessels for the required residence time and with the necessary stages to effect the desired wax crystal growth, by direct contact with boiling liquid refrigerant. Cooling is achieved by the injection of the liquid refrigerant into a horizontal vessel or vessels. The petroleum oil stock is fed into the crystallizer vessel or first vessel in a series at a temperature condition corresponding to that of complete solubility of the wax in the oil feed. A dewaxing solvent may be introduced in addition to the petroleum oil stock and dissolved therein. Agitation is applied by the boiling liquid refrigerant to facilitate instantaneous mixing of the oil and solvent, and to achieve thorough heat and mass transfer between the two liquid surfaces. If desired, mechanical agitation may be utilized in conjunction with the agitation supplied by the boiling liquid refrigerant. Agitation is required to achieve heat transfer and offset the deleterious effects of local areas of shock chilling and failure to achieve a uniform cooling rate. With certain stocks or operations the quantity of boiling refrigerant to achieve the required heat removal may be inadequate to produce the needed agitation. Under these circumstances mechanical agitation would be employed to supplement that from the boiling refrigerant.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a flow diagram of the dewaxing process. FIG. 2 is a detailed diagram of the crystallizer chamber contemplated in the present process.

DETAILED DESCRIPTION

Referring to FIG. 1, a petroleum distillate fraction is fed from the oil storage tank 1 through lines 2 and 8 into the crystallizer chamber 9. If desired, a dewaxing solvent may be added, being fed from the solvent storage tank 3 either through lines 4 and 5, where it is mixed with the oil feed in line 6, or through line 10 directly to the crystallizer 9. The oil, or the oil-solvent mixture, may also be heated in the heater 7 prior to entry into the crystallizer chamber 9 which may consist of one or more vessels. If more than one vessel is employed, these may be connected by piping in a parallel or series sequence. In the crystallizer chamber 9, the autorefrigerant is added through line 24 and inlet pipe 25, and the chamber is maintained at a pressure such that the autorefrigerant boils on contact with the oil feed stream therein. Vaporized autorefrigerant is withdrawn through line 14, pressurized, condensed and recycled through lines 24 and 25. The dewaxed oil-wax mixture or dewaxed oil-wax-dewaxing solvent mixture is withdrawn through line 15, and each component therein is separated therefrom. This may be accomplished by passing the dewaxed oil mixture into a means 28 for separation of the liquid and solid portions thereof. The solid portion, or wax slurry, then passes through line 30 into a high pressure flash tower 32, for separation of autorefrigerant, and then into a low pressure flash tower 39 for separation of the dewaxing solvent. The final wax product may then be recovered through line 42, or may be subjected to further purification if desired. The liquid portion recovered from the separation means 28 passes through line 29 into a high pressure flash column 31 for separation of autorefrigerant, and then into low pressure flash tower 38 for separation of the dewaxing solvent. The final dewaxed oil product may then be recovered through line 43, or may be subjected to further purification if desired. Autorefrigerant recovered from these flash towers is condensed and recycled through line 37 to the autorefrigerant storage tank 23, and dewaxing solvent recovered from the flash towers is condensed and recycled through lines 48 and 50 to the solvent storage tank 3.

The petroleum distillate fractions employed in this process will have an initial boiling range of from between 400°F. to 1,500°F., an initial wax content of from about 1.0 to about 25.0 wt. %, preferably from 15.0 to 25.0 wt. %, and initial pour and cloud points of from about 40°F. to 130°F. and 45°F. to 140°F., respectively. The preferred oil stocks are the lubricating oil and specialty oil fractions, boiling within the range of from 420°F. to 1,300°F., having initial pour and cloud points of from 85°F. to 120°F. and 90°F. to 130°F., respectively. These petroleum oil fractions may come from any source, such as the paraffinic crudes obtained.
from Aramco, Kuwait, the Panhandle, North Louisiana, Tia Juana, Western Canada, etc. The dewaxing solvent which may be employed in conjunction with the present invention includes the ketones from C₄ to C₆, such as methyl ethyl ketone (MEK), acetone, methyl isobutyl ketone (MIBK), methyl propyl ketone (MPK) and mixtures thereof, as well as mixtures of these ketones with aromatic compounds, such as benzene and toluene and mixtures thereof. Certain solvent mixtures are preferred, such as methyl ethyl ketone (MEK) and methyl isobutyl ketone (MIBK), and methyl ethyl ketone (MEK) and toluene, etc.

When such a solvent is employed, it may be fed from the solvent storage tank 3 through lines 4 and 5, where it will be mixed with the oil feed in line 6. However, if the temperature and pressure in the first stage or stages of the crystallizer are such that appreciable vaporization of the solvent will take place, then the solvent may be fed from the solvent storage tank 3 to the crystallizer through line 10. The solvent flowing through this line may be heated or cooled in exchanger 11 to 50°F. to 180°F. and then fed to the crystallizer at the required stage or stages. The oil feed is maintained at a temperature such that the wax therein is completely dissolved, that is, such that none of the wax therein is in the crystalline form, and the oil, or oil-solvent mixture, is above its congealing point. Thus, where the oil has a relatively low wax content, the oil, or oil-solvent mixture, may be fed into the crystallizer chamber 9 at storage temperatures; but where the oil has a relatively high wax content, the oil, or oil-solvent mixture, will have to be heated in order to obtain the desired feed. The temperature of the oil, or oil-solvent mixture, will generally be from 120°F. to 180°F. prior to its entry into the crystallizer chamber 9 through line 8. In addition, where a dewaxing solvent is employed, it will be utilized in amounts such that it will be fed into the crystallizer chamber at from 50 to 1,500 bbl/hr.; however, it will be apparent to those skilled in the art that higher or lower feed rates may be utilized. These solvent feed rates will result in solvent/oil ratios of from between 1.5 to 6.0, and preferably from 3.0 to 5.0. It is additionally noted that where the oil and solvent enter in virtually complete admixture, improved filterability of the wax slurry may be obtained.

The autorefrigerant employed in conjunction with this invention will enter the crystallizer chamber 9 through line 24 and inlet pipes 25 through control devices 26, and will be dispersed therein through a dispersion means 52, referring to FIG. 2. The autorefrigerant employed will be liquid, normally gaseous hydrocarbons from C₂ to C₄, such as propane, propylene, ethane, ethylene, C₂ hydrocarbons and mixtures thereof. These hydrocarbons, in their liquid state, will generally be at from -50°F. to about 130°F. immediately prior to their entry into the crystallizer chamber.

The crystallizer chamber 9 itself is a chamber wherein the two liquid phases, namely oil, or oil-solvent, and autorefrigerant, are permitted to come into direct contact with each other. It will be of a size such that, at given feed rates, there will be an additional vapor space above the liquid phase. Preferably, the chamber will be so arranged that the liquid phase may pass therethrough in a given direction, i.e., downstream, and the temperature of the oil will gradually decrease as it passes in that direction. The chamber will be provided with a control device(s) 26 which will allow for the controlled flow of autorefrigerant into the vessel, and exit lines 13, for the autorefrigerant vapors to escape therefrom. It is preferred that the exit will contain a means 12 for controlling the pressure inside the crystallizer chamber. The crystallizer chamber may consist of a multiplicity of vessels to achieve the above results. These vessels may be arranged in parallel or series or a suitable combination thereof. Where the stages are in more than one vessel, these shall be connected with a suitable arrangement of pipes to permit the oil, wax solvent and dissolved autorefrigerant to flow from the last stage of one vessel to the first stage of the next vessel. This arrangement is required where the vessels are in series. Separate piping will provide for the introduction of autorefrigerant and the release of vapors through lines 13.

The pressure thus achieved inside the crystallizer chamber 9 is directly related to the pour point of the dewaxed oil product which is ultimately obtained. Thus, as the pressure at this point is increased from atmospheric upwardly, the pour point of the final product will also be increased. Generally, the pressure within the chamber will be from about 1 to about 100 psig, and preferably from 1 to 35 psig.

The chilling rate employed in conjunction with the present invention will be from about 1°F. to 10°F./minute, and preferably from between about 1°F. to 5°F./minute. As factors in the choice of chilling rate to be employed, it must be borne in mind that as the chilling rate is lowered, the filterability of the slurry improves, and a higher yield of oil is recovered, that is, there is less occlusion of oil in the wax crystals. But, as the chilling rate is lowered, larger equipment will be required, with concomitantly higher costs.

Within the crystallizer, the oil or oil-solvent feed, and autorefrigerant will thus be at conditions such as soon as the autorefrigerant contacts the warmer oil or oil-solvent feed it will begin to boil, or vaporize. The rate of boiling will be directly proportional to the pressure, which will in turn be controlled by the control device 12. This device 12 will additionally control the final pour point of the product obtained at line 15. For example, if a final pour point of 25°F. is desired, the pressure produced in the vapor space 9(a) by the pressure control device 12, will be from between 30-35 psig, where propylene is the autorefrigerant utilized, and acetone is used as a dewaxing solvent; while if a final pour point of -25°F. is desired, the pressure will be approximately 1 psig, that is, slightly above atmospheric pressure.

These conditions are somewhat dependent on the solvent/oil ratio. For a given oil or solvent/oil feed the final temperature obtained by adjusting the pressure within the crystallizer governs the pour point of the dewaxed oil product. Variations in flow and temperature of the feed to the crystallizer, as long as corrected by a change in the autorefrigerant flow, do not affect this pour point.

As the two crystallizer feed streams are contacted in the chamber 9, the autorefrigerant vapors leaving overhead through line 14 will be at a temperature of
between $-50^\circ$ and $180^\circ$F., preferably between $-50^\circ$ and $80^\circ$F., and will contain from between 0 to 60.0 wt. % dewaxing solvent, preferably from 0 to 40.0 wt. % dewaxing solvent. This vapor will then be cooled to a temperature such that any dewaxing solvent entrained therein will be condensed, but to a temperature above that at which the autorefrigerant will condense. This will generally correspond to temperatures of from between 70$^\circ$ to 130$^\circ$F. The autorefrigerant vapors, which are now essentially pure, are then compressed, condensed and recycled.

The wax slurry, wax-oil or wax-oil-solvent mixtures, which are withdrawn from the crystallizer chamber 9 through line 15, will have an oil/wax ratio of from between 3.0 to 5.0 where a dewaxing solvent is not employed. When a dewaxing solvent is employed, this mixture will contain from between 4.0 and 20.0 wt. % wax, and between 50.0 and 80.0 wt. % dewaxing solvent. This liquid-solid mixture will then be separated utilizing a means 28 which allows the liquid phase to pass therethrough, but prevents passage of the solid phase or wax. Thus, some type of filtration device may be utilized. In addition, the liquid and solid phases may be separated by a centrifugal device. Where a filter is employed, the filtration temperatures employed will be from about between $-50^\circ$ to about 25$^\circ$F.

The liquid phase, oil and autorefrigerant, or oil, autorefrigerant and dewaxing solvent, as well as the predominately solid phase, wax and autorefrigerant and dewaxing solvent, will then each be separated by separation processes known in the art, such as fractionation, stripping, etc. Prior to separation, these two streams will generally have the following compositions: (1) liquid stream 15.0 to 35.0 wt. % dewaxed oil, 0 to 85 wt. % autorefrigerant and 0 to 85 wt. % dewaxing solvent, (2) solid stream 10 to 100 wt. % wax, 0 to 80 wt. % autorefrigerant and 0 to 85 wt. % dewaxing solvent.

The final dewaxed oil which is recovered from line 43, will have from 0 to 0.01 wt. % dewaxing solvent therein, preferably 0 to 0.003 wt. % dewaxing solvent, 0 to 0.01 wt. % autorefrigerant, will contain from 0 to 0.01 wt. % wax dissolved therein and will have pour and cloud points of between $-50^\circ$ and 30$^\circ$F., and $-45^\circ$ and 35$^\circ$F. respectively, preferably between $-10^\circ$ and 10$^\circ$F. and $-5^\circ$ and 15$^\circ$F. respectively.

**PREFERRED EMBODIMENT**

Referring again to FIG. 1, a petroleum oil fraction boiling between 420$^\circ$ and 1,300$^\circ$F., containing between 15.0 and 25.0 percent wax, and having initial pour and cloud points of between 85$^\circ$ and 120$^\circ$F. and between 90$^\circ$ and 130$^\circ$F. respectively, is fed from the oil storage tank 1 through line 2 where it is mixed with the dewaxing solvent, i.e., acetone. The acetone is fed from the solvent storage tank 3, where it is kept at storage temperatures of from 50$^\circ$ to 130$^\circ$F., through lines 4 and 5. The oil is fed through line 2 at from between 100 to 1,000 barrels/hour, and the acetone is fed through line 4 at from between 50 to 1,500 barrels/hour, thus resulting in a flow rate of from between 150 to 2,500 barrels/hour in line 6, and an oil/acetone ratio therein of between 1.5 and 2.0.

The oil-solvent feed is heated in the heater 7 by steam or fuel gas to a temperature of between 130$^\circ$ and 180$^\circ$F., so that all wax contained in the oil is completely dissolved. This mixture is then fed into the crystallizer chamber 9 through line 8.

Referring to FIG. 2, the crystallizer chamber will consist of from 10 to 30 stages, arranged in horizontal vessel or vessels, each stage of which will contain a liquid space 9(b) and a vapor space 9(a), and will be separated from one another by baffles 51 arranged so that both these spaces are partitioned and thus the liquid phase may flow downstream from one stage to the next, but is prevented from flowing upstream. Each stage contains a means 52 for dispersing the liquid autorefrigerant within the liquid space, in order to provide better contact between the autorefrigerant and the oil or oil-solvent feed. This means 52 may be a distributor or sparger. In addition, each stage may contain means 44 for the additional mechanical agitation of the liquid phase, such as an impeller, which will be connected to a drive means or motor 45. The vapor space within each stage will contain an exit line 13 fitted with a pressure valve 12 to regulate the pressure therein. Where the stages are in more than one vessel, these shall be connected with a suitable arrangement of pipes to permit the oil, wax, solvent and dissolved autorefrigerant to flow from the last stage of one vessel to the first stage of the next vessel. This arrangement is required where the vessels are in series. Separate piping will provide for the introduction of autorefrigerant and the release of vapors through lines 13.

Referring again to FIG. 1, the oil or oil-solvent mixture is cooled at a rate of between 3.0$^\circ$ and 4.0$^\circ$F./minute, as it passes through the chamber, by direct contact with the boiling autorefrigerant, i.e., propylene, which provides agitation and mixing within the liquid phase. The propylene, at between $-50^\circ$ and 130$^\circ$F. and between 1 and 310 psig enters the crystallizer chamber 9 through lines 25 which is fitted with control valves 26. The vaporized propylene, containing between 0 and 40.0 percent acetone, passes overhead through pressure valve 12 and line 13 and collects in line 14, from which it passes into a condenser 17, where the vapors are cooled by heat exchange with water to between 70$^\circ$ and 130$^\circ$F., at which point the acetone vapors condense, and are collected in line 16 and recycled to the solvent storage tank 3. The first stage of compression may precede cooling in condenser 17. This acetone stream may be further purified, if desired, by means known in the art. The relatively pure propylene vapors are then compressed in the compressor 19 containing from between one to three stages, to a vapor at a higher pressure, namely, from between 30 to 340 psig. This vapor then passes through line 20 into the condenser 21 wherein it is cooled by heat exchange with a coolant such as water or air to a temperature of between 50$^\circ$ and 130$^\circ$F., and this liquid propylene then passes through line 22 into the autorefrigerant storage tank 23, from which it may be recycled through line 24 back into the crystallizer chamber 9.

The wax slurry produced in the crystallizer chamber 9 consists of between 5.0 and 25.0 wt. % wax, between 0 and 85.0 wt. % propylene and between 0 and 85.0 wt. % acetone. This slurry passes from the crystallizer chamber 9 through control valve 27 and line 15 into the rotary vacuum filter 28 where the liquid and solid phases are separated, that is, the wax crystals collect on
the filter drum, and are removed by means known in the art such as a doctor blade, etc. with the aid of a filter blow gas, and the filtrate consisting of between 15.0 and 30.0 wt. % dewaxed oil, between 0 and 85.0 wt. % propylene and between 0 and 85.0 wt. % acetone, passes theretofrom through line 29. The waxy cake, containing between 0.0 and 4.0 wt. % dewaxed oil occluded in the wax crystals, and between 0 and 80.0 wt. % propylene and between 0 and 80.0 wt. % acetone passes through line 30 into a high pressure flash tower 32, maintained at a temperature of between 100°C and 350°C, and a pressure between 205 and 240 psig, so that the overhead vapors thus consist of propylene vapors at between 100°C and 110°C, and between 200 and 230 psig, which may be further cooled and purified and recycled to the autoclave storage tank 23. The liquid phase leaving the bottom of the high pressure flash tower 32 passes through line 36 where the acetone is separated from the molten wax at a lower pressure of between 6 and 8 psig, and a temperature of between 230°C and 450°F in the low pressure flash tower 39. The acetone in the vapor phase leaves the top of the low pressure flash tower 39 through line 41 and into line 48 where it is condensed and recycled to the solvent storage tank 3. The molten wax withdrawn from the bottom of the low pressure flash tower 39 will contain between 5 and 25.0 wt. % occluded dewaxed oil, between 0 and 0.01 wt. % propylene, and between 0 and 0.01 wt. % acetone. Further purification may be carried out if desired.

The dewaxed oil-propylene mixture passes from the rotary vacuum filter 28 through line 29 into the high pressure flash column 31, which is maintained at a pressure of between 28 and 32 psig, and a temperature of between 235°C and 450°F, and thus wherein the propylene entrained therein will be flashed overhead through line 33 and recycled to the autoclave storage tank 23. The liquid phase withdrawn from the bottom of the high pressure flash column 31 through line 34 will consist of dewaxed oil and acetone at a temperature of between 420°C and 450°F, and will pass into the low pressure flash tower 38, maintained at a lower pressure of between 5 and 7 psig, at a temperature of between 225°C and 450°F, and having from seven to 21 stages, and wherein the acetone will be flashed overhead through line 40, condensed and recycled and the liquid phase dewaxed oil will be withdrawn through line 43 at a temperature of between 400°C and 440°F, and containing a final pour and cloud point of between 0°F and 10°F, and 5°F and 15°F, respectively. This final dewaxed oil will contain from 0 to 0.01 wt. % propylene and from 0 to 0.01 wt. % acetone. Further purification may be carried out if desired utilizing means well known in the art.

Example 1

The process of the present invention is carried out in a horizontal crystallizer vessel containing 20 stages, which are baffled, and each of which contains a pressure valve above the vapor space thereof. A waxy Mid Continent type petroleum distillate fraction, boiling at 750°F, having an initial pour and cloud point of 90°F and 130°F, respectively, and a wax content of about 20 percent is utilized, being fed into the crystallizer vessel at a rate of 250 Bbl/Hr. The autoclave employed is propylene, and it is used in conjunction with a dewaxing solvent, namely acetone. An oil/solvent ratio of 0.5:1.0 is employed. The acetone and oil streams are thoroughly admixed prior to entry into the crystallizer vessel, and heated to a temperature of 130°F, so that all the wax contained in the oil feed is thoroughly dissolved therein. The propylene is then fed into the first stage of the crystallizer at the aforementioned rate, and at a temperature of 100°F, and a pressure of 205 psig, and begins to boil in contact with the warmer oil. The pressure in this vessel is maintained at 7 psig, in order to achieve the boiling of the autorefrigerant, and the resultant cooling of the waxy oil feed. The oil is cooled at a rate of 3.5°F/minute, and the slurry withdrawn from the final stage is at a temperature of 35°F and contains 10.0 wt. % precipitated wax crystals. The wax crystals are separated from the dewaxed oil in a rotary filter, and the wax which is recovered, after the removal of solvent by distillation, contains 15.0 wt. % oil occluded thereon. The dewaxed oil is purified by removing solvent therefrom by distillation, and the final product has pour and cloud points of 0°F and 5°F respectively.

What is claimed is:
1. A continuous process for dewaxing a waxy petroleum oil stock comprising introducing said oil stock into a chilling vessel that is divided into a plurality of stages, introducing incrementally along the length of the chilling vessel a liquid refrigerant into at least a portion of said stages, maintaining the pressure in each of said stages such that at least a portion of said refrigerant vaporizes on contact with said petroleum oil stock thereby cooling it and precipitating at least a portion of said wax from said oil, maintaining a high degree of agitation in at least a portion of said stages so as to effect substantially instantaneous mixing of said oil stock and said refrigerant, removing a slurry containing said petroleum oil stock and precipitated wax, separating said precipitated wax from said petroleum oil stock, and recovering wax and a petroleum oil stock of diminished wax content.
2. The process of claim 1 wherein the liquid refrigerant is selected from the group consisting of C₃-C₄ hydrocarbons and mixtures thereof.
3. The process of claim 1 wherein the said petroleum oil stock is cooled at a rate of about 1°F-10°F per minute.
4. The process of claim 2 wherein the refrigerant is selected from the group consisting of propane, propylene, ethane, ethylene and C₄ hydrocarbons and mixtures thereof.
5. The process of claim 1 wherein said petroleum oil stock is a lubricating oil boiling within the range of from about 400°F to 1,500°F.
6. A continuous process for dewaxing a waxy petroleum oil stock comprising introducing said oil stock into a chilling vessel that is divided into a plurality of stages, introducing incrementally along the length of the chilling vessel a liquid refrigerant selected from the group consisting of C₃-C₄ hydrocarbons and mixtures thereof into each of said stages, controlling the pressure in each of said stages such that at least a portion of said refrigerant vaporizes on contact with said oil stock thereby cooling it at a rate of about 1°F-10°F per minute as it progresses through the vessel and
thereby precipitating at least a portion of said wax from said oil, maintaining a high degree of agitation in each of said stages so as to effect substantially instantaneous mixing of said oil stock and said refrigerant, separating precipitated wax from said petroleum oil stock, and recovering a petroleum oil stock of diminished wax content.

7. A continuous process for dewaxing a waxy petroleum oil stock comprising mixing said oil stock with a dewaxing solvent and introducing said mixture into a chilling vessel that is divided into a plurality of stages, introducing a liquid refrigerant incrementally along the length of the chilling vessel into at least a portion of said stages, controlling the pressure in each of said stages such that at least a portion of said refrigerant vaporizes on contact with said oil stock thereby cooling it and precipitating at least a portion of said wax from said oil, maintaining a high degree of agitation in at least a portion of said stages so as to effect substantially instantaneous mixing of said oil/solvent mixture and said refrigerant, separating said precipitated wax from said petroleum oil stock, and recovering a petroleum oil stock of lower wax content.

8. The process of claim 7 wherein the chilling vessel contains from about ten to thirty stages.

9. The process of claim 7 wherein the dewaxing solvent is selected from the group consisting of \( C_5-C_8 \) ketones, mixtures thereof and mixtures of \( C_5-C_8 \) ketones with aromatic compounds, and the liquid refrigerant is selected from group consisting of \( C_5-C_8 \) hydrocarbons and mixtures thereof.

10. The process of claim 9 wherein the cooling rate is about 1°-10°F per minute.

11. The process of claim 9 wherein the dewaxing solvent is selected from the group consisting of methyl ethyl ketone, acetone, methyl isopropyl ketone, methyl isobutyl ketone and mixtures thereof.

12. A continuous process for dewaxing a waxy petroleum oil stock comprising introducing said oil stock into a chilling vessel that is divided into a plurality of stages, introducing incrementally along the length of the chilling vessel a dewaxing solvent and a liquid refrigerant into at least a portion of said stages, maintaining the pressure in each of said stages such that at least a portion of said refrigerant vaporizes on contact with said oil stock thereby cooling it and precipitating at least a portion of said wax from said oil, maintaining a high degree of agitation in at least a portion of said stages so as to effect substantially instantaneous mixing of said oil stock, dewaxing solvent and refrigerant, separating said precipitated wax from said petroleum oil stock and solvent, and recovering a petroleum oil stock of lower wax content.

13. The process of claim 12 wherein the dewaxing solvent is selected from the group consisting of \( C_5-C_8 \) ketones, mixtures thereof and mixtures of \( C_5-C_8 \) ketones with aromatic compounds, and the liquid refrigerant is selected from group consisting of \( C_5-C_8 \) hydrocarbons and mixtures thereof.

14. The process of claim 13 wherein the cooling rate of said petroleum oil stock is about 1°-10°F per minute.

15. The process of claim 1 wherein a high degree of agitation effecting substantially instantaneous mixing of the oil stock and the refrigerant is maintained in each of the stages in the chilling vessel.

16. The process of claim 7 wherein a high degree of agitation effecting substantially instantaneous mixing of the oil/solvent mixture and the refrigerant is maintained in each of the stages in the chilling vessel.

17. The process of claim 12 wherein a high degree of agitation effecting substantially instantaneous mixing of the oil stock, dewaxing solvent and refrigerant is maintained in each of the stages in the chilling vessel.

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